

b25

(12) UK Patent Application (19) GB (11) 2 324 273 (13) A

(43) Date of A Publication 21.10.1998

(21) Application No 9810767.5

(22) Date of Filing 07.08.1995

Date Lodged 19.05.1998

(30) Priority Data

(31) 06208199	(32) 10.08.1994	(33) JP
(31) 06210727	(32) 12.08.1994	
(31) 07100043	(32) 31.03.1995	

(62) Divided from Application No 9516173.3 under Section 15(4) of the Patents Act 1977

(51) INT CL⁶
B43L 1/00

(52) UK CL (Edition P)
B6P PMAB

(56) Documents Cited
None

(58) Field of Search
UK CL (Edition P) B6P PMAB
INT CL⁶ B43L 1/00
Online databases: EDOC, WPI

(71) Applicant(s)

Chemitech Inc
(Incorporated in Japan)
2-8-33 Wakamatsu-cho, Fuchu-shi, Tokyo 183, Japan

(74) Agent and/or Address for Service

Boult Wade Tennant
27 Fenchurch Street, LONDON, EC4A 1PO,
United Kingdom

(72) Inventor(s)

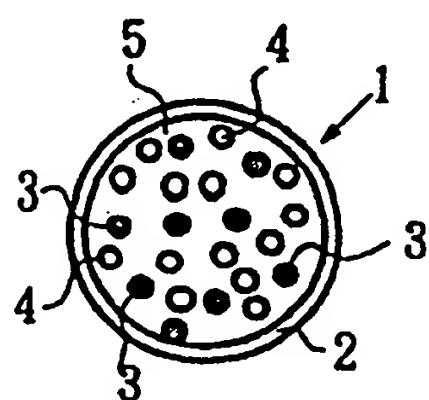
Takashi Iwasaki
Sadatoshi Igau
Atushi Ogura

(54) Abstract Title

Gelatinised microcapsules for magnetic display sheets

(57) Gelatinised microcapsules 1 for magnetic display sheets containing magnetic powder 3 and non-magnetic powder 4, comprise a dispersion medium 5 composed of low boiling point solvent, optionally with a high boiling point solvent (>175°C), the average particle diameter of the microcapsules being in the range 200-800 µm.

FIG 1



GB 2 324 273 A

FIG. 1

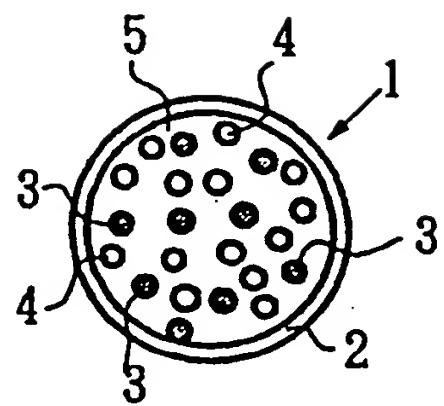
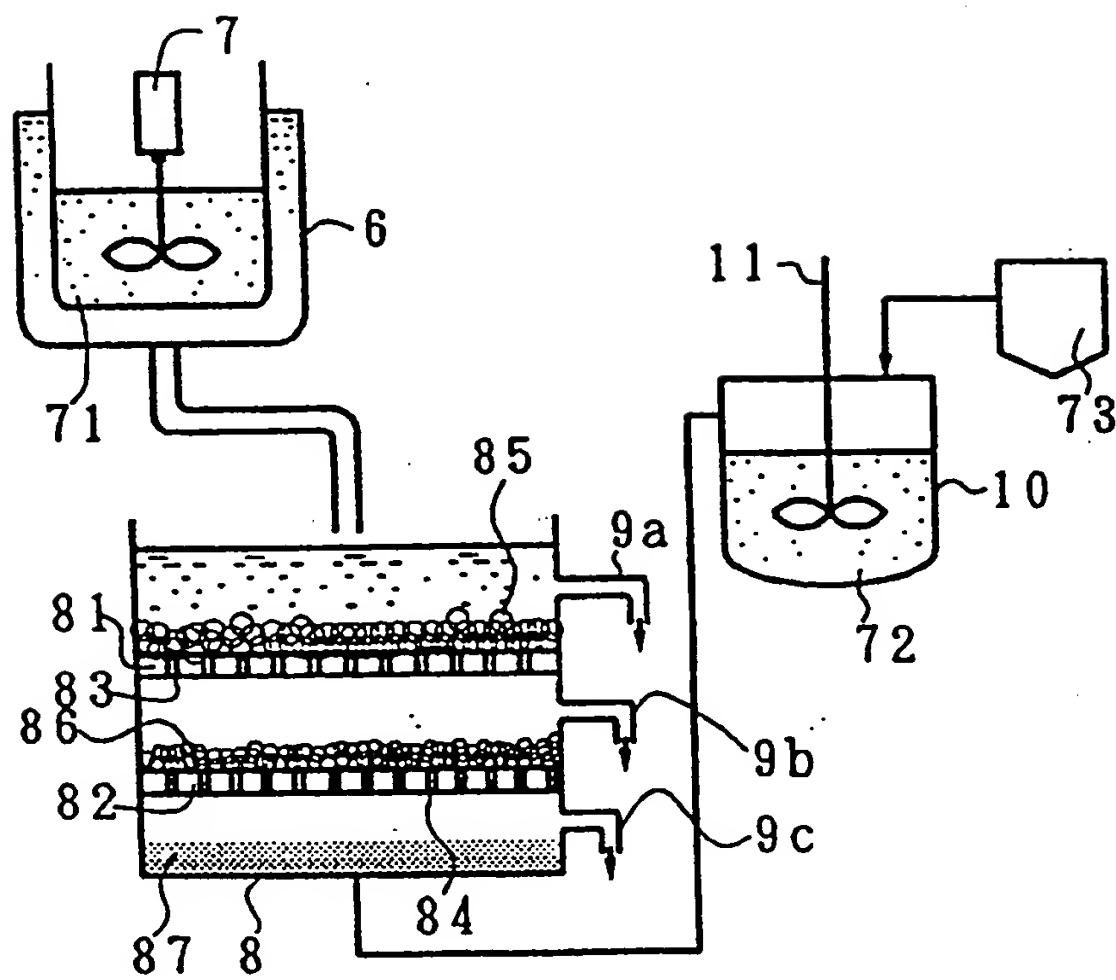


FIG. 2



2/5

FIG. 3A

COATING STEP

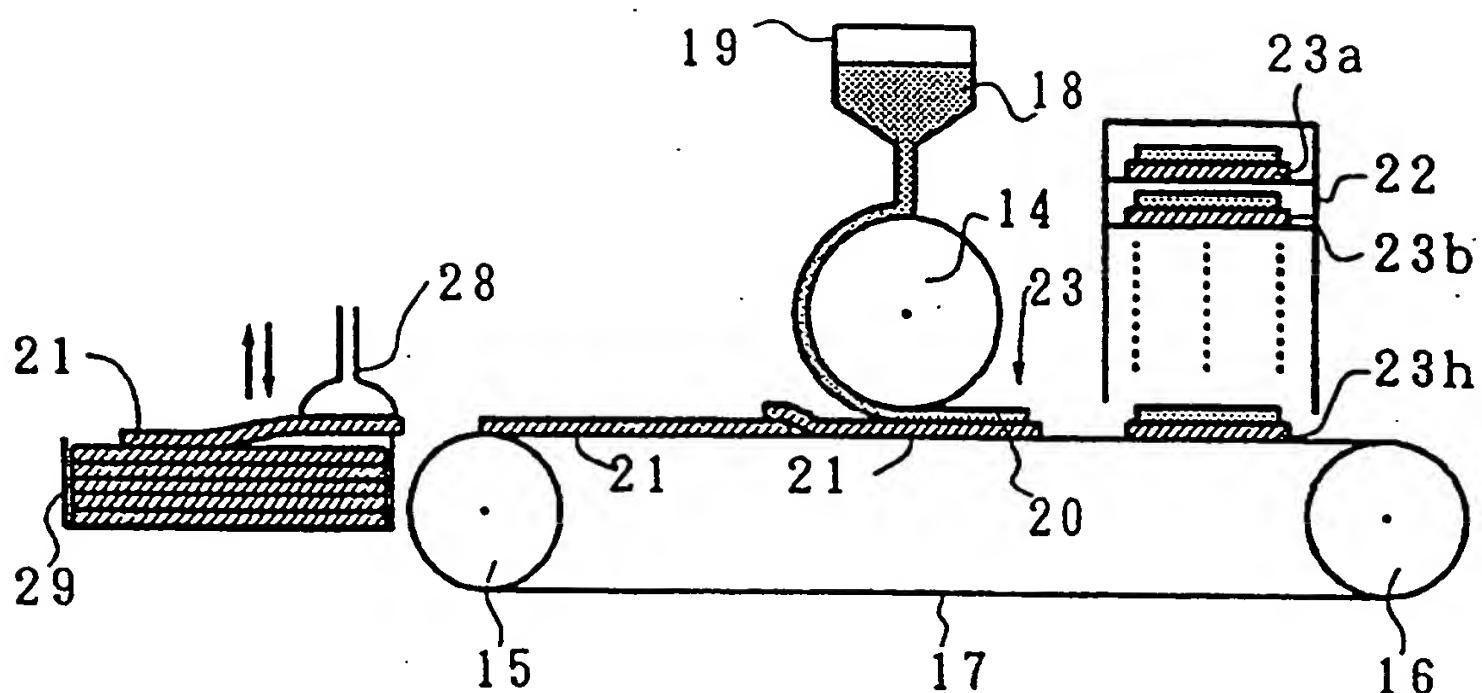


FIG. 3B

DRYING STEP

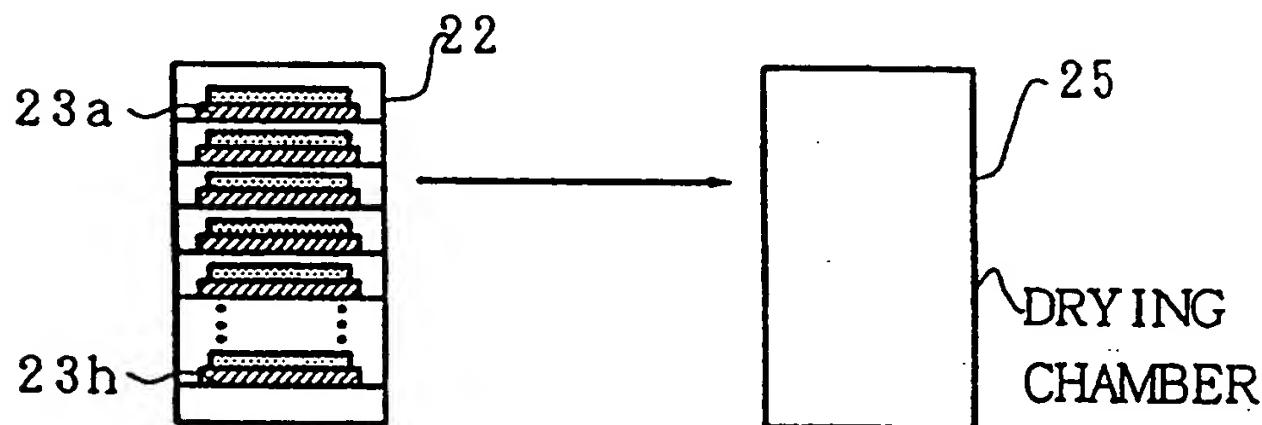
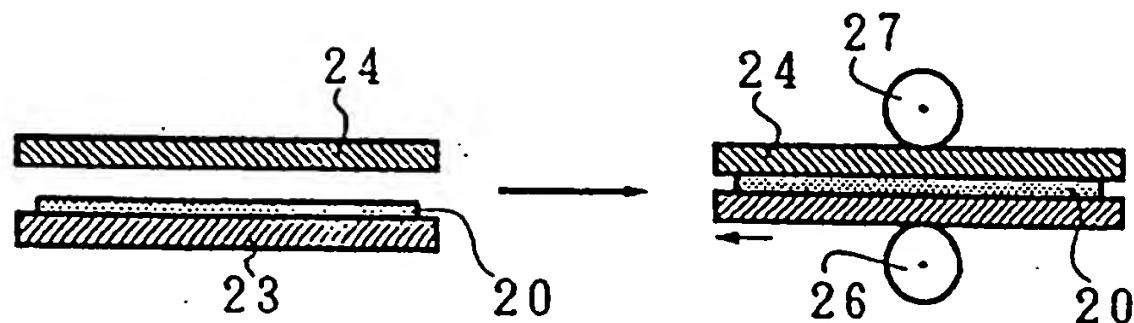


FIG. 3C

LAMINATING STEP



3/5

FIG 4

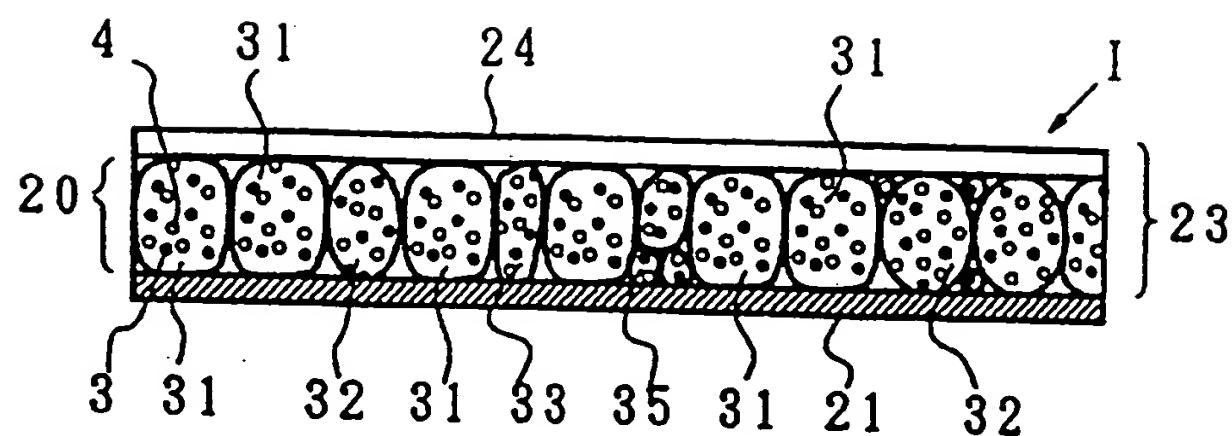


FIG 5A

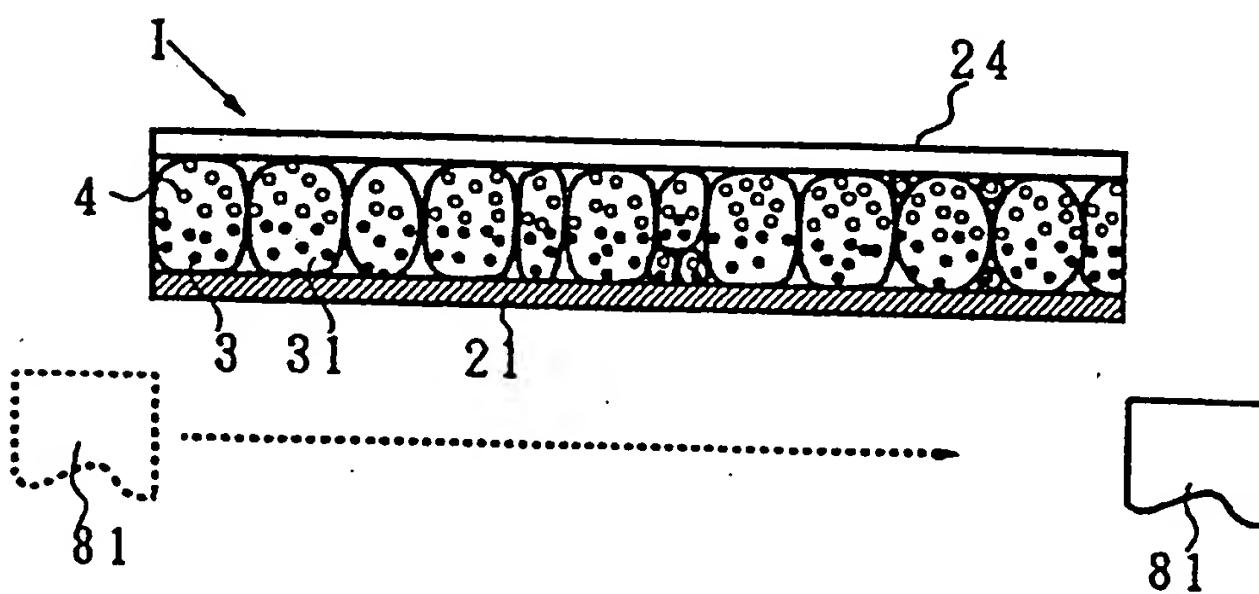


FIG 5B

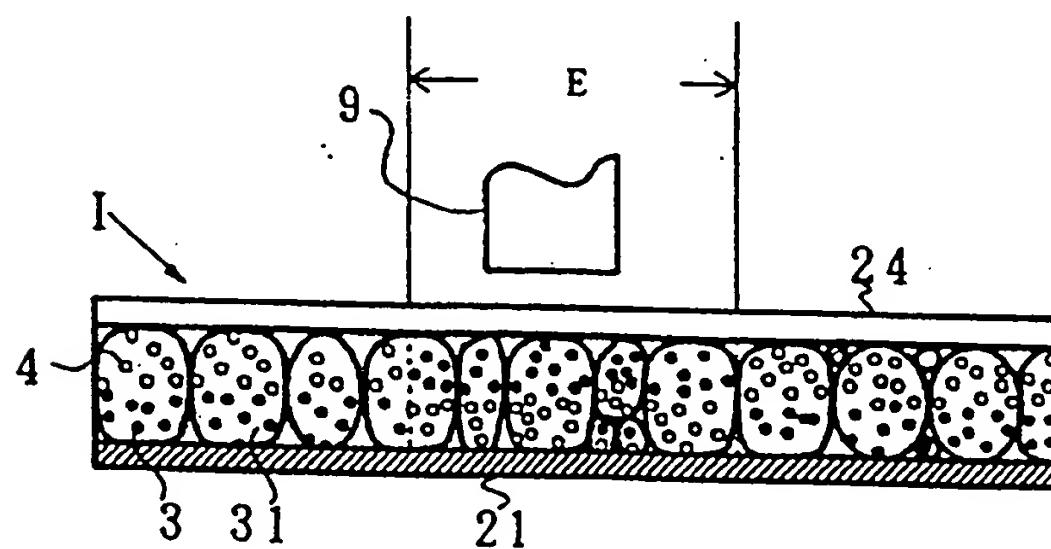


FIG 6

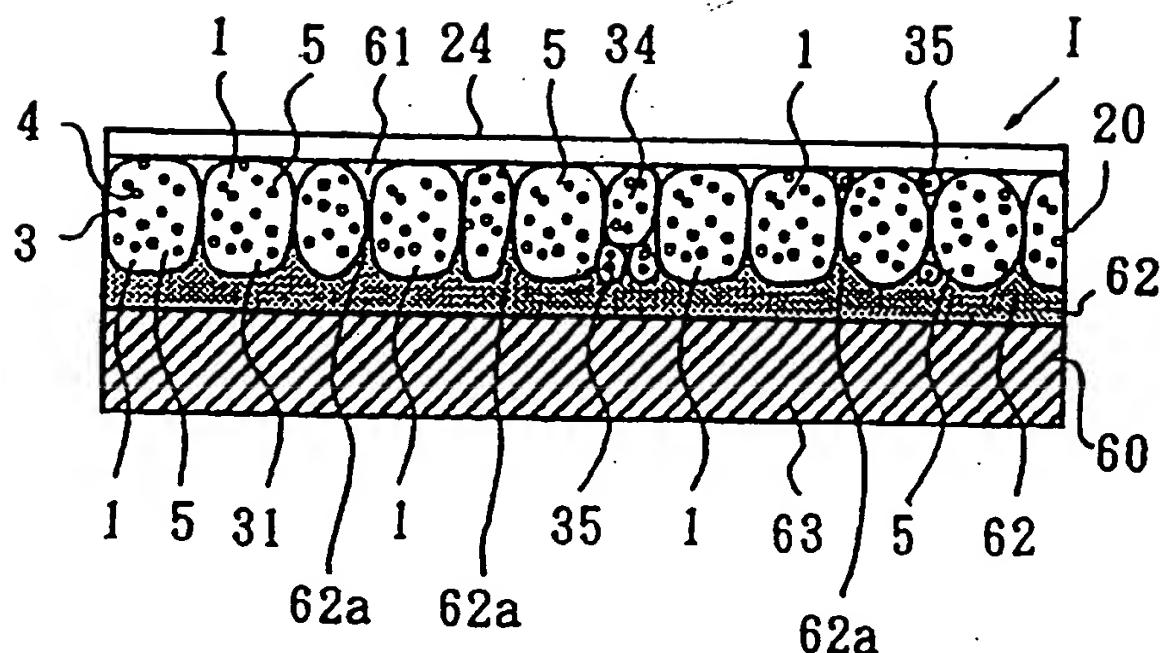
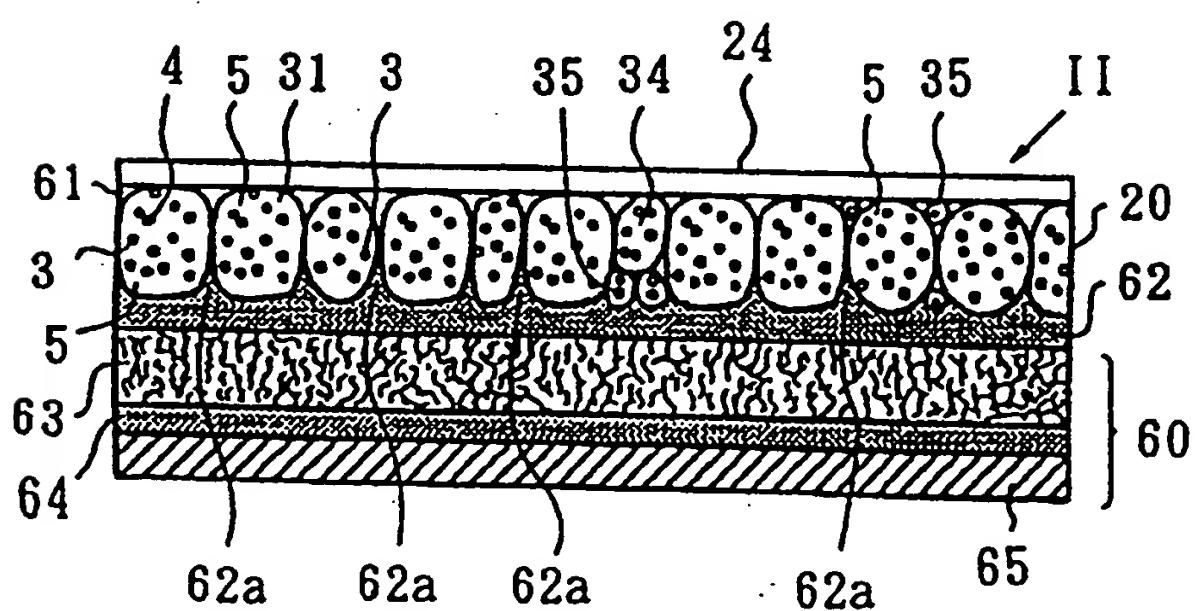


FIG 7



5/5

FIG 8

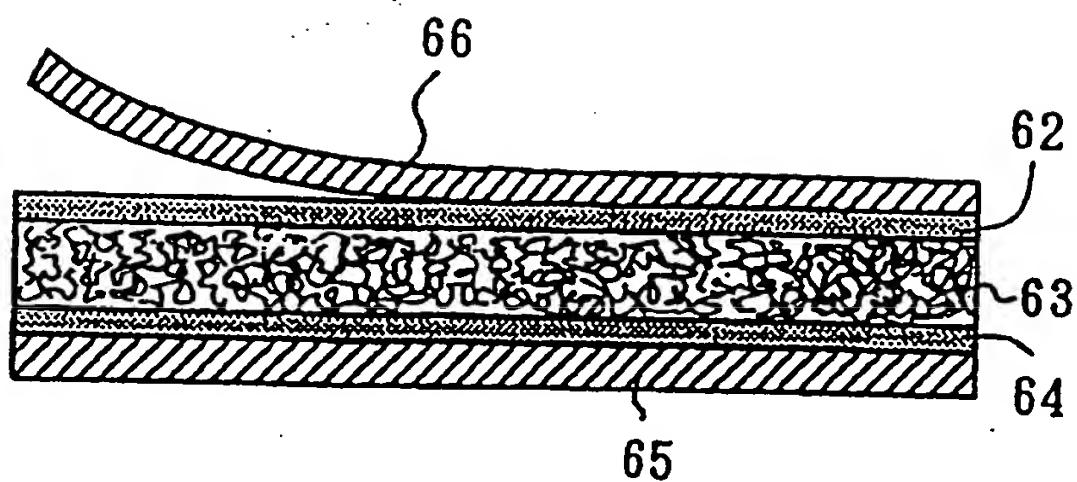
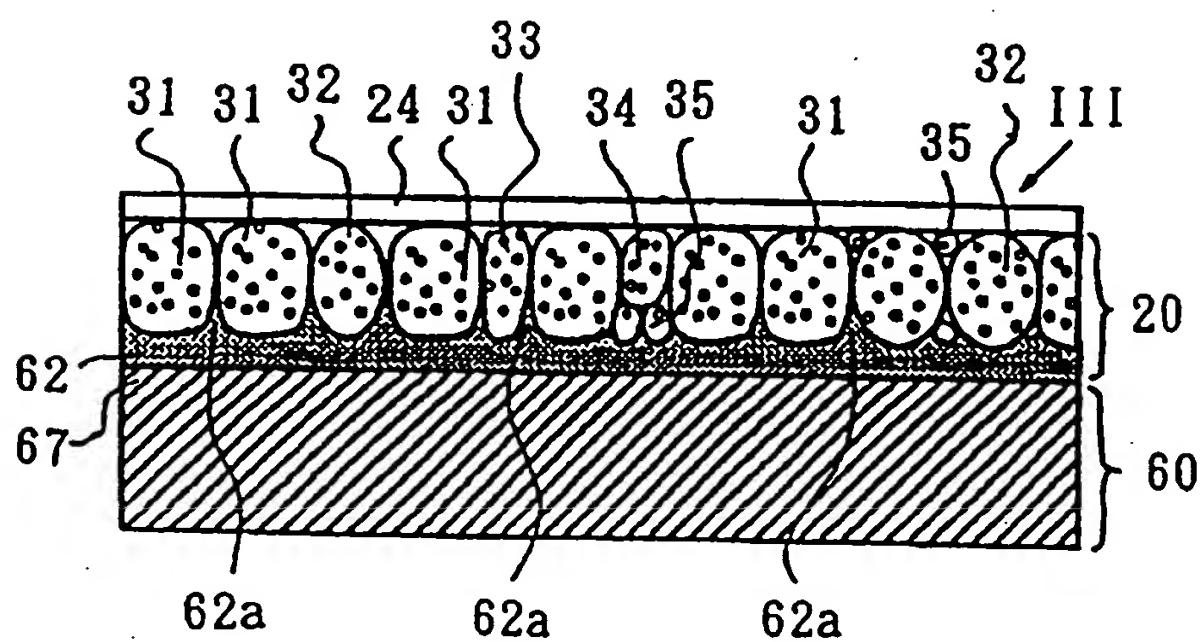


FIG 9



2324273

MICROCAPSULES FOR MAGNETIC DISPLAY

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to Gelatinized microcapsules for magnetic display in which dispersion medium, magnetic powder and nonmagnetic powder are enclosed.

DESCRIPTION OF THE PRIOR ART

Many methods in magnetic display are well known so far, for example, a magnetic display method that makes small rooms between two plates, seals ball-shaped magnetic powder and tungsten oxides particles in liquid in the small rooms and makes display by moving the magnetic powder to surface by magnetic force (So-called as moving type as below) was published in Japanese Patent Publication Kokoku S51-10959. And inventions published in Japanese Patent Publication Kokoku S57-27463, S59-31710, S59-47676 and S62-53359 have made a improvement of the dispersion medium in order to make a good dispersion of the magnetic powder and the tungsten oxides particles. Among them, there is a invention about a magnetic display system in practical use that makes small rooms with size of 4 mm³ having honeycomb shape on a supporting plate, injects liquid with white pigment and magnetic powder therein in the honeycombs and laminates and seals a transparent sheet on it to make it finished.

According to this display system, a display may be made by scanning a magnet on back surface of the magnetic display plate from one side to the opposite so as to attract the magnetic powder in the honeycombs to the back surface and to make the surface white. While making contact of permanent magnetic pen with the surface of the magnetic display, the magnetic powder in the contact part move to the surface and image appears.

On the other hand, in Publication of Japanese Patent Publication Kokoku S54-29895, a magnetic record medium that is produced by coating microcapsules having sensitive flakes in it that have sensitivity to magnetic field and are floating in liquid on a base plate is described. According to this invention, when a magnetic field brings to bear on the magnetic record medium, the sensitive flakes in the microcapsules are oriented to perpendicular direction, only a part of the sensitive flakes is under the magnetic field, moves in longitudinal direction, orients to horizontal to the magnetic record medium and shows image (so-called as deflection type as below). The same magnetic display method by the magnetic flakes are also published in Publication of Japanese Patent Application Laid-open S63-153197, S64-19384 and H1-145637. The two types of moving type and deflection type are also published in Publication of Japanese Patent Publication Kokoku S55-29880. In the magnetic display system using ball-shaped magnetic powder, a invention according to which a better display may be made by specifying

size of microcapsules and mixing two kinds of microcapsules with different sizes is described in Japanese Patent Publication Kokoku H4-233581.

There are some problems among the inventions published up to now particularly in Japanese Patent Publication Kokoku H4-233581. The magnetic display method by using microcapsules consisting of the ball-shaped magnetic powder in it can not be put into practical use, because although a good display may be made, but the image are not clear and recording speed and erasing speed are slow when the magnetic force is weak.

Further, the microcapsule particles may be destroyed gradually while writing repeatedly by a magnetic pen so clearness of the display sheet falls down. Durability of the display sheet has to be improved.

Therefore, the inventors of the invention have conducted many researches and discovered that the durability of microcapsule magnetic display sheet depends on thickness and hardness of the transparent film and arrangement of cushion element (pressure-proofing film) adjacent to the microcapsule dispersoid and the destroy of the microcapsules caused by pressure is relieved by the thickness and hardness of the transparent film.

SUMMARY OF THE INVENTION

According to the above circumstances, it is a first object

for particular embodiments of the invention to provide gelatinized microcapsules for magnetic display that can record words or pictures in high clearness and with high record speed under a weak magnetic force lower than 1100 gauss.

The gelatinized microcapsules for magnetic display may be _____ characterized in that the dispersion medium in the microcapsules being composed of low boiling point solvent and the size of the microcapsules in average being $200 \mu m$ to $800 \mu m$. The microcapsules _____ have the merits of displaying speed and erasing speed being rapid words and pictures recorded by them being very clear while use.

Furthermore, microcapsules having particle diameter bigger than the average diameter are removed from. Thus, when ink is produced by mixing the microcapsules with binders and is painted on a base plate in thickness of $800 \mu m$, uncleanness caused by big microcapsules disappears. And, it is clarified that when the microcapsules are formed essentially in size of $400 \mu m \pm x \mu m$ to $800 \mu m \pm x \mu m$ ($x=10\text{--}20$), a clearer words or pictures may be recorded.

The dispersion of the low boiling point solvent from the capsule film can be prevented by mixing solvents with boiling

point higher than 175°C into the low boiling point solvent.

Addition and dispersion of dispersant in dispersion medium makes the magnetic powder and nonmagnetic powder uniform and long-keeping. As the magnetic powder are kept in this station for a long time with stability by adding suspension in the dispersion medium, the words or pictures formed can be kept for a long time correspondingly. Furthermore, the magnetic and nonmagnetic powder may be moved under a weak magnetic force as that are affinity-treated.

After adding arabic gum in the capsuled mixture, good microcapsules are formed by reducing PH to acidity and cooling it below 20°C to form the gelatin/arabic gum membrane.

Eliminating water from the prepared microcapsules to form condensed liquid containing microcapsule slurry and condensation in 40% to 70% is desirable. Dispersing the condensed microcapsules in aqueous transparent adhesives to form ink and then coating the ink on a transparent base film. One of microcapsule dispersoid or pressure-proofing film may be colored. Pigment may also be added in the microcapsules or membrane in necessary.

By removing the particles bigger than average, uncleanness caused by destroy of the big particles may not occur. Dispersing the microcapsules from which the big particles are removed out in aqueous transparent adhesives. The

particles in $200 \mu m \pm x \mu m$ to $200 \mu m \pm x \mu m$ ($x=10-20$) are desirable..

Viscosity of the microcapsule dispersoid is desirable to be suitable for coating on the base film. The viscosity will be different depending on season. After regulating it to 15,000cp to 35,000cp, coating it on base film and then drying it to prepare microcapsule coating layer.

The microcapsule magnetic display sheet has an order of pressure-proofing film, microcapsule dispersoid and transparent film. As the microcapsule dispersoid are supported by the pressure-proofing film, the destroy of the microcapsules in the microcapsule dispersoid caused by writing pen is prevented and recorded words or pictures are kept for a long time in good clearness.

The method of producing microcapsule magnetic display sheet are composed of the processes of coating microcapsule dispersoids containing magnetic powder and nonmagnetic powder and dispersion medium on a transparent film, drying it to form microcapsule dispersoid layer, adhering a pressure-proofing film having a adhesive layer thereon to the surface of the dispersoid layer. So the pressure-proofing film is filled to the concave parts of the uneven surface of the dispersoid layer firmly without gaps (vapor bubbles) to form an adhesive part.

Examples of low boiling point solvent which can be used in the gelatinized microcapsules for magnetic display are:

))
benzene, ethylbenzene, toluene, o-xylene, m-xylene, p-xylene, mesitylene, cumene, methyl cyclohexane, ethyl cyclohexane, dibutyl ether, 2-pentanone, 3-pentanone, 2-hexanone, methyl isobutyl ketone, heptane, octane, nonane, 4-heptanone, 1-pantanole, butyl acetate, isobutyl acetate, isopentyl acetate etc. Among them, toluene, o-xylene, m-xylene, p-xylene, methyl cyclohexane, ethyl cyclohexane, butyl acetate, isobutyl acetate, isopentyl acetate etc. are the most usable in the invention. One kind or a mixture of two kinds of them are usable.

Example of high boiling point solvent which has a boiling point higher than 175°C and which can be used in certain embodiments of the present invention are:
1-pantanole, 1-octanole, 2-octanole, 2-ethyl-1-hexanole, 1-nanonole, 3,5,5,-trimethyl-1-hexanole, benzyl alcohol, 1,2-propane diol, 1,3-butanediol etc. 1-octanole, 2-ethyl-1-hexanole, 3,5,5-trimethyl-1-hexanole, benzyl alcohol are the most usable. While mixing the low boiling point solvent with the solvents with boiling point higher than 175°C, _____ toluene and 1-octanole, toluene and 2-ethyl-1-hexanole, toluene and 3,5,5-trimethyl-1-hexanole, toluene and benzyl alcohol, xylene (o-xylene, m-xylene, p-xylene) and 1-octanole, xylene and 2-ethyl-1-hexanole, xylene and 3,5,5-trimethyl-1-hexanole, xylene and benzyl alcohol are the desirable mixtures. While the boiling point of the solvents with high boiling point being

lower than 175°C, a bad influence on the actions of the magnetic powder may occur. The reasons for that can be considered as that boiling point of the solvents with high boiling point is so similar to that of the low boiling point solvent as viscosity and volatility of the dispersion medium can not be suppressed. In preferred embodiments, mixtures of low boiling point — solvent and solvents with high boiling point are used as the dispersion medium and mixtures of solvents with high boiling point with toluene or xylene, further mixtures of alcohol compounds with toluene or xylene are desirable.

Polyoxyethylene laurylether, polyoxyethylene cetylether, polyoxyethylene stearyl ether, polyoxyethylene oleil ether, anion fatty group ester mixtures and amine polycarbonate may be pointed out as the dispersant used in the invention to disperse the magnetic powder. Quantity of the dispersant used is the same as traditional of 0.5% to 10% in weight, the most suitable one is 1.0% to 3.0% in weight. If the quantity of the dispersant is less than 0.5% in weight, no good effect may be made and if it is more than 10% in weight, the viscosity of the dispersant is going so high as the characteristics of the dispersant may be destroyed.

In particular embodiments, in the case of solvents with boiling point lower than 175°C, a bad influence on the action of the magnetic powder occur. The reason for that may be considered as the boiling point is so near to that of solvents

with low boiling point as the viscosity and volatility are restrained.

While mixtures of the low boiling point solvent and that with boiling point higher than 175°C are used,

the quantity used of the solvents with high boiling point is desirable to be 20 % to 250 % of the quantity of the low boiling point solvent in weight and 50 % to 150 % in weight are most desirable. While rate of the quantity of the solvents with high boiling point to that of the low boiling point solvent being less than 20 %, the dispersion of the low boiling point solvent can not be prevented and while that being more over than 250 % in weight the action of the magnetic powder will become worse.

Absolute silicic acid, water-bearing silicic acid, sodium silicate, silicates (sodium silicate, kalium silicate, aluminum silicate, calcium silicate etc.), alumina fine powders, silica powders, siliceous earth, kalion, hard clay, soft clay, bentinite, calcium carbonate fine powders, activated potassium carbonate fine powders, calcium hydrogencarbonate, calcium water-bearing alkali magnesium carbonate, barium sulfate, benzidine yellow may be pointed out as the precipitation-prevention agents. One kind or mixtures of two kinds of them are usable. The adding quantity of the suspension to the dispersion medium is different depending on the dispersion medium, 0.2 % to 5% of the dispersion medium in weight is general, 0.4% to 2% in weight is the most desirable. If the quantity

of the suspension is less than 0.2%, no good precipitation-preventing effects may be desirable, and if the quantity is more than 5% in weight, the suspension may be an obstacle to the actions of the magnetic powder.

The magnetic powder used _____ are the traditional one well-known in the technical field, for example, black iron oxide, magnese dioxide-bearing iron oxide, chromium dioxide, ferrite, iron or nickel fine powders, iron-nickel alloy etc. One or mixture of two kinds of them may be used. In order to mix the magnetic powder with other elements easily, the magnetic powder sold on market are affinity-treated. TODACARA-KN-320 in trademark, magnenite made by TODA INDUSTRY INC. and TAROKKUSU BL-220 in trade mark, composite iron oxide made by CHITAN INDUSTRY INC. may be the example. Particle diameter of the magnetic powder is desirable to be smaller than $10 \mu m$, $.01 \mu m$ to $5 \mu m$ may be more desirable and 0.1μ to $0.3 \mu m$ are the best. _____ While the particle diameter of the magnetic powder being over than $10 \mu m$, such problems as the clearness of words being worse and the response displaying and erasing speed being low will occur. And while the particle diameter being smaller than $0.1 \mu m$, the magnetic powder will condense and not disperse. Titanium dioxide, rutile pigments may be pointed out as the nonmagnetic powder used in particular embodiments. No limit to the particle diameter

of the nonmagnetic powder so long as they can be dispersed enough.

0.1 μ to 1 μ m may be good and big particles are not desirable as light shading decreases.

Colorants may be added in the dispersion medium of the microcapsules or the gelatin membrane in particular embodiments so the magnetic display sheet may be colored. Usual pigments and dyestuffs, specially aqueous pigments may be used as the colorants. Such dyestuffs as methylene blue, Congo red, benzo-yellow and such pigments as oil blue, oil green, oil yellow, benzidine yellow, new lactisum (made by DAINISEI CHEMISTRY INC.) are desirable.

In preferred embodiments the magnetic and nonmagnetic powder are desirable to be affinity-treated. Silicon may be a better affinity-treating agent. The affinity treatment makes them easily moving. Surfaces of the magnetic and nonmagnetic powder are treated with water-bearing metal oxides so as to make them affinity-having. Aluminum, silicon, titanium, zinc, zirconium etc. may be pointed out as the metals by which the water-bearing metal oxides may be made. For example, mixture of $Al_2O_3 \cdot nH_2O$ and $SiO_2 \cdot nH_2O$ is a water-bearing metal oxide, in which Al_2O_3 has lipophilicity and SiO_2 makes hydrophilicity. By changing content of Al_2O_3 and SiO_2 the lipophilicity may be changed to hydrophilicity if necessary and therefore the magnetic and nonmagnetic powder may be moved under a weak magnetic force.

Quantity of the water-bearing metal oxides used may be 1% to 16% of the magnetic or nonmagnetic powder in weight and 3% to 10% may be better. The particle diameter of the gelatinized microcapsules for magnetic display —————— may be 200 μm to 800 μm in average and 400 μm to 800 μm may be better. While particles bigger than average being used, the magnetic display sheet has no durability as the microcapsule themselves are not strong. And, when the microcapsules containing big particles are painted on a base film, the paint surface is not smooth and big particles are destroyed by case, for example while coating thickness of 800 μm , the particles bigger than 800 μm may be destroyed, therefore a clear picture may not be obtained. So it is desirable to remove the big particles out. Filter or fine gip through which only small particles can pass may be used for removing the big particles. Furthermore, a thin magnetic display sheet and clear words or pictures may be made by the microcapsules with diameter $400 \mu\text{m} \pm x \mu\text{m}$ to $800 \mu\text{m} \pm x \mu\text{m}$ ($x=10 - 20$).

The gelatinized microcapsules for magnetic display —————— may be colored. Traditional pigments and dyestuffs may be used as the colorants. Water-soluble pigments are desirable. The gelatinized microcapsules for magnetic display —————— show words or pictures under a magnetic force after dispersed into binders and painted on a base film so as

to form a magnetic display sheet. Any traditional method for displaying the words or pictures that are well known in the field may be used. Using particular embodiments, when a magnet bigger than 1100 gauss is used for recording or erasing, displaying and erasing speed is fast and words or pictures recorded are clear and no changes occur even a magnet smaller than 1100 gauss used. In general magnet with 1100 to 700 gauss may be used for recording words or pictures, 1000 to 800 gauss may be better and there is no difficulty if a magnet weaker than that is used. A magnet with 200 to 300 gauss may also be used for erasing the recorded words or pictures with fast speed. Therefore gelatinized microcapsules for magnetic display —————— are much more economic and technique. Usual coating methods, for example, brush coating, roller coating, screen coating, air curtain method, dip coating etc. may be used for coating the microcapsules on the base film.

The pressure-relieving element for magnetic display sheet using certain embodiments may be composed of flexible cushion with thickness of $50 \mu\text{m}$ to $500 \mu\text{m}$, $200 \mu\text{m}$ to $400 \mu\text{m}$ is better. Unweaved cloth, synthetic resin film, elastic materials, for example, gum material, foamy materials etc. may be used, synthetic resin film with adhesive layer or unweaved cloth with the adhesive layer are more desirable. The unweaved cloth with the adhesive layer may be protected by a synthetic film on its backsurface. Thickness of the unweaved cloth is desirable to

be not thick from the view point of erasing, 250 μ m to 500 μ m is good. the adhesive layer of the unweaved cloth is 30 μ m to 130 μ m. A lot of kinds of adhesives may be used. For example, they can be made by adding adhesives, softening agent, aging-preventing agent, packing materials in elastomers of natural gum, isoprene gum, styrene, butadiene gum, styrene butadiene copolymer, styrene isoprene block copolymer, tetyl gum, polyisobutylene, silicone gum, polyvinyl isobutyl ether, chloroprene gum, nitrile gum, graft gum, reproduced gum etc. The natural gum, styrene-butadiene series, acryl series and silicone are desirable.

Such natural fiber as silk cotton, linen, jute, wool, silk, cellulose fiber such as rayon, acetate, polyamide fiber as nulon, chlorinated hydrocarbon fiber as vinylidene and synthetic fiber as acryl fiber, polyurethane fiber, polypropylene fiber may be used as the unweaved cloth. The unweaved cloth may be made of the fibers mentioned above by a traditional method. While using the unweaved cloth, front surface, namely surface having microcapsule dispersoids thereon, and back surface are better to have films. Polyethylene terephthalate (as: PET as below), polyethylene film, polypropylene film, chlorovinyl film, polyester film, polycarbonate film may be used as the films. The film may be adhered by adhesives and thickness of them is 50 μ m to 200

μ m.

While using the synthetic resin film having adhesive layer as the pressure-relieving element, the adhesive layer plays very important role, namely, adhering the synthetic film having adhesive layer thereon to the microcapsule dispersoid layer. The adhesives are desirable to adhere the surface of the microcapsules and no gap exists between them so flexibility of the magnetic display sheet (Strength against bending) can be improved. From the view point of protecting microcapsules and erasing recorded words easily thickness of the adhesive layer is not desirable to be too big, 30 μ m to 130 μ m is general. While the thickness of the adhesive layer being thinner than 30 μ m, microcapsules can not be protected enough and destroyed possibly by pressure of pen. While it is thicker than 130 μ m, even the microcapsules may be protected but recorded words can not be erased enough. It is not economic to use a strong magnet for erasing.

In certain magnetic display sheets comprising microcapsules embodying the present invention the thickness of the synthetic film is 50 μ m to 200 μ m. From the same view point as the above-mentioned, 100 μ m to 180 μ m is desirable. Natural gum, styrene-butadiene series, polychloroprene series, polyisoprene series, polyurethane series, acryl series and silicone may be pointed as the adhesives. Polyethylene terephthalate, polyethylene film, polypropylene film,

chlorovinyl film, polyester film, polycarbonate film are the examples of the synthetic film used also in back surface of the unweaved cloth.

After preparing microcapsules containing magnetic powder, nonmagnetic powder and dispersion medium, dispersing them into aqueous emulsion adhesives. Painting the prepared microcapsule dispersoid on a transparent base film, drying it to form microcapsule dispersoid paint layer. The transparent film plays roles as relieving pressure to microcapsules to protect them from destroy. Relieving pressure to the microcapsules means the transparent film may not be bent or injured and its flexibility are not destroyed under the writing pressure. Hardness of the transparent film depends on thickness of it. Polyethylene terephthalate, polyethylene transparent film may be used but they are not the all. Thickness of the film may be $30 \mu m$ to $250 \mu m$ and $50 \mu m$ to $150 \mu m$ is better. Method of Painting the microcapsule dispersoids on the film are traditional, for example, brush coating, roller coating, screen coating, air curtain, dip coating. After coating process, drying process follows and then laminating the pressure-proofing film on the surface of dispersoids.

The magnetic display sheet are made by the method described as follow. Namely, gelatinized microcapsules for magnetic display are made by processes (I) to (III) then the magnetic display sheet are made by the processes (a) to (e).

(I) A process of adding magnetic, nonmagnetic powder and dispersion medium into the gelatin aqueous solution at temperature of 20°C to 60°C and stirring them, most desirable coacervation may be obtained by the process. The order to add the magnetic, nonmagnetic powder and dispersion medium is optimal, order of magnetic powder, nonmagnetic powder then dispersion medium is good, order of nonmagnetic powder, magnetic powder then dispersion medium, order of dispersion medium, magnetic powder then nonmagnetic powder or dispersion medium, nonmagnetic powder then magnetic powder are all no problem. But, the order of mixing magnetic powder and nonmagnetic powder in the dispersion medium and then adding to the gelatin aqueous solution is the most desirable.

(II) A process of forming gelatin/arabic gum polymer membrane by adding arabic gum aqueous solution into the mixture above-obtained, reducing PH to acidity (preferably lower than PH4) and then cooling it to the temperature lower than 20°C,

(III) A process of forming the gelatinized microcapsules by hardening the gelatin/arabic gum polymer membrane.

(a) A process of removing the particles bigger than average diameter and then eliminating water from the gelatinized microcapsules prepared above. It is desirable to eliminate the water from the prepared microcapsule slurry to keep the mixture with suitable viscosity while forming a mixture of the gelatinized microcapsules and binders. In this process, the

microcapsules are arranged in average diameter or microcapsules in average diameter are used and particles bigger than that are removed. In order to remove the particles bigger than average diameter, a sieve may be used. By removing the particles bigger than average and only the microcapsules passed through the sieve used, a paint layer may be kept in a good thickness, nonnative microcapsules are removed so a clear record on the display sheet may be obtained. The removing process can also be conducted with coating process. For example, setting a gap between the surface and roller and only the unbroken particles passed through the gap may be painted on the surface.

(b) A process of preparing microcapsule dispersoids by dispersing microcapsules obtained above into aqueous transparent adhesives. As the dispersoids are desirable to have a good viscosity while coating, the viscosity of the dispersoids have to be regulated to 15,000cp to 35,000cp in this process. Sodium alginate, polyvinyl alcohol, modified sodium polyacrylate, modified polyacrylic acid emulsion and modified polyacrylic acid sulphate etc. may be pointed out as the viscosity regulators and the sodium alginate and polyvinyl alcohol are more desirable. Rate of the viscosity regulators depends on season's temperatures and conditions of dispersoids and 0.5% to 3.0% of the dispersoids in weight is general. While the viscosity of the dispersoids being lower than 15,000cp, cracks of painted film may occur and records are not clear. And

while the viscosity of the dispersoids being higher than 35,000cp, the painted film are not uniform and uneven.

(c) A process of coating the dispersoids on a transparent base film. Polyethylene terephthalate, polyethylene transparent film may be the examples used as the base film but they are not the all. Thickness of the films are 100 μ m to 250 μ m and 150 μ m to 200 μ m are desirable. As methods for coating the microcapsule dispersoids on the films mentioned above, brush coating, roller coating, screen coating, air curtain method, dip coating etc. may be used. After coating, drying process follows. Drying temperature may be in traditional range, for example in 40°C to 120°C, 50°C to 90°C are desirable. Drying time is usually 30 min. to 50 min. Warm wind drying or convection drying are desirable as the drying methods. The thickness of the microcapsule dispersoids after drying is desirable to be 400 μ m to 600 μ m.

(d) A process of laminating a pressure-proofing film on the dispersoids paint layer. The pressure-proofing film is not limited and polyethylene terephthalate (PET) may be good. The thickness of the polyethylene terephthalate is desirable to be 100 μ to 250 μ m.

The magnetic display sheet or magnetic display medium
can record words or pictures with
a magnet. Methods for recording words or pictures on the

magnetic display sheet or medium are well known in the technical field. Any of them may be used. And the described magnetic display sheet or medium may be used in a wide range, for example, picture books and toys for children, word-trainer, game-board, memo board, blackboard for meeting, memo board for clean room, photo-electric notice board etc.

Using a preferred embodiment, —— as the low boiling point solvent are used in the dispersion medium capsuled in microcapsules, displaying speed is fast even using a weak magnet. And a more clear words or pictures may be recorded as only the microcapsules in $200 \mu\text{m}$ to $800 \mu\text{m}$ are used. By removing the particles bigger than average uncleanness caused by destroy of the big particles on coating is prevented. Because microcapsules in $400 \mu\text{m} \pm x \mu\text{m}$ to $800 \mu\text{m} \pm x \mu\text{m}$ ($x=10 \sim 20$) are formed essentially, more clear words or pictures are recorded. And, solvents with boiling point higher than 175°C are mixed in the low boiling point solvent, dispersion of the low boiling point solvent may be prevented. And, by adding and dispersing emulsifiers in the dispersion medium, the magnetic and nonmagnetic powder are dispersed uniformly and kept for a long time in stable condition. Furthermore, by adding suspension in the dispersion medium the magnetic powder may be kept in displaying condition for a long time therefore the words or pictures recorded are very stable. By lipophilicity-treating

the magnetic and nonmagnetic powder, they can be moved by a weak magnetic force.

The microcapsule dispersant layer of the magnetic display sheet produced by using the above-described microcapsules are supported by the pressure-proofing films. Therefore, the display sheet is strong against writing pressure so destroy of the microcapsules caused by the writing pressure is prevented. The sheet has a good durability so words displayed by the sheet can be kept for a long time in high clearness.

As the described microcapsule display sheet is composed of mainly unweaved cloth as its base film to support microcapsule dispersoid, destroy of the microcapsules in the microcapsule dispersoids is prevented by the flexibility and cushion of the unweaved cloth. So the described sheet has good durability and can be repeatedly used for a long time with keeping clearness of the formed pictures.

In a preferred embodiment of the microcapsule display sheet, as adhesives with a fixed thickness stick firmly to uneven surface of the microcapsule dispersoid with no gap between them by using synthetic film having an adhesive layer thereon as the base film supporting the microcapsule dispersoids, the flexibility of the magnetic display sheet is good and the destroy of the microcapsules in the dispersoids is prevented by thickness and flexibility of the adhesive layer. Therefore, the magnetic display sheet as the same as the unweaved cloth has good

durability and may be used repeatedly for a long time.

The pressure-proofing film is adhered firmly on surface of microcapsule dispersoids having adhesive layer with no gap between them .

On the other hand, while preparing the magnetic display sheet, a clear record without cracks on the painted film and unevenness may be obtained by regulating the viscosity of the microcapsule dispersoids. Furthermore, the microcapsule destroy may be prevented by laminating a pressure-proofing film. Aqueous pigments may be added into at least one of the components of the described display sheet so as to color it.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1 is a cross-sectional view of gelatinized microcapsule for magnetic display;

Fig.2 is a flow sheet of preparing gelatinized microcapsule dispersoid;

Figs.3A to 4C are cross-sectional views of coating equipment for manufacturing the magnetic display, in which Fig.3A shows coating process, Fig.3B shows drying process and Fig.3C shows laminating process;

Fig.4 is a cross-sectional view of the magnetic display sheet;

Figs.5A to 5C are cross-sectional views of writing word on the described magnetic display sheet in which , Fig.5A shows a magnet scanning on backsurface of the magnetic display sheet

and Fig.5B shows a magnetic pen writing a word on the surface of the magnetic display sheet;

Fig. 6 or Fig. 9 is a cross-sectional view of another magnetic display sheet;

Fig.7 is a cross-sectional view of one example of a pressure-proofing film of the magnetic display sheet; and

Fig.8 is a cross-sectional view of another pressure-proofing film of the magnetic display sheet.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention may be described in more detail as follow but the examples here are only used for describing the invention and not makes limitation to the invention.

Example 1

The gelatinized microcapsules for magnetic display used _____ are illustrated in Fig.1, a cross-sectional view, _____ and made by the method described below. In Fig.1, microcapsules I enclose magnetic powder 3 and nonmagnetic powder 4 that are dispersed in dispersion medium 5 in a capsule membrane 2 which is formed by gelatin in the microcapsules I, the magnetic powder 3 are ferrite powders 2% in weight (TAROKUSU BL-220 made by CHITAN INC.) with diameter of 0.3 μm in average and their surfaces are also treated by silicon oil.. Adding the magnetic powder and nonmagnetic powder in a mixture solvents 85% in weight of toluene and 2-ethyl-1hexanole in mixture ratio 5:3, adding PERENOLE E1(silicone

made by SANOPOKO INC.) 0.2% in weight as defoaming agents and silicic acid powders (AEROJIRU972 made by Japan AERJIRU INC.) 0.5% in weight as suspension and then adding ammonium polycarbonate (RAKIKUERU963 made by SANOBUE INC.) 0.7% in weight as interfacial agents and dispersing them to produce the microcapsules.

Then, adding arabic gum aqueous solution with concentration 1.8 into gelatin aqueous solution with concentration 1.8% that is regulated to be PH6 to prepare aqueous solution for microcapsule membrane, heating it to 50°C, regulating ti to PH=5 and pouring the dispersion medium with magnetic powder 3 and nonmagnetic powder prepared above and stirring until drops of the dispersion medium become 600 μ m. After the desirable dispersion medium obtained, adding water being 4 times of gelatin, cooling it slowly and the cooling it to 10°C, gelatinizing polymer membranes of gelatin/arabic gum separated on the interface, adding glutar aldehyde aqueous solution with concentration 25%, hardening the polymer membranes, then the gelatinized microcapsules I are prepared completely. Removing particles bigger than 600 μ m from the gelatinized microcapsules I prepared by the method described above, particles smaller than 600 μ m are obtained. The microcapsules prepared above being 400 μ to 600 μ are 85%.

Fig.2 is a flow sheet of preparing the described

dispersoids of the gelatinized microcapsules 1. According to the slow sheet, adding above-mentioned components in a temperature controllable tank 6 with a stirrer 7, stirring, regulating temperature and PH as that mentioned above to prepare the microcapsules. The prepared microcapsule slurry 71 are introduced to filtrating equipment 8, particles bigger than 600 μ m 85 and water are removed by filter 81 and only the particles smaller than 600 μ m are remained on filter 82. Water flows out from spouts 9a, 9b and 9c. There are holes 83 can not pass and there are holes 84 in the filter 82 through which fine particles 87 can pass. Then, in order to prepare paint ink 72, the prepared microcapsules 86 are introduced to a container 10 with a stirrer 11 and aqueous urethane resin are added and stirred as the aqueous binder 73. the prepare paint ink 72 is painted by a coating equipment as shown in Fig.3. The viscosity of the paint ink 72 is 28,000cp.

Fig.3 is a cross-sectional view of the coating equipment for preparing the magnetic display sheet. Fig.3A shows coating process. In Fig.3A, the coating equipment is rotating along arrow by belt conveyer 17 and roller 15 and 16. Attraction element 28 that moves up and down from the film supplying equipment 29 attracts the transparent film 21 and transport it to the belt conveyer 17. The film inserts to a transported film 21 and piles up in head part. The paint ink 18 made of microcapsule dispersoids in the tank 19 are painted on the film

by roller 14. The painted sheet 23 are collected in a rack 22 and placed as 23a, 23b, ... 23h. Fig.3B shows drying process. Rack 22 is put into a drying room 25 and dried for 40 min. by warm wind. Fig.3C shows laminating process, a PET film as pressure-proofing film is laminated on the surface of the painted sheet 23 by adhesives and then the magnetic display sheet is finished.

Fig.4 is a cross-sectional view of magnetic display sheet I prepared by the described method and gelatinized microcapsules.

In Fig.4, after the above-prepared microcapsules I are dispersed in binders, they are painted on a PET film 21 to form a microcapsule paint layer 23 and then, a PET film as a pressure-proofing film is adhered to the paint layer by adhesives. The microcapsules are arranged suitably in the magnetic display sheet I. In stead of PET film 21, glass fiber, glass, paper, other hard sheet or soft flexible film that have strength enough to protect the microcapsules 20 may be used.

A method to display words on the magnetic display sheet II made of gelatinized microcapsules _____ will be described in detail as follows. Fig.5 is a cross-sectional view for describing the method on the magnetic display sheet II. Fig.5A shows that a magnet is scanning on the backsurface of magnetic display sheet II and Fig.5B shows that a magnetic pen is writing the capital E on the surface of the sheet. At first, a weak magnet sheet 8 (200 gauss) is used for scanning along

the arrow on the pressure-proofing film 6 of the magnetic display sheet II as shown in Fig.4 to move the magnetic powder 3 in the microcapsules I to the pressure-proofing film 6 (Erasing Operation). Because the magnetic powder 3 in the microcapsules exist only near to the pressure-proofing film 6 of the display sheet II and not in the record film 7 and only the nonmagnetic powder exist in it, the surface of the display sheet II is as white as the nonmagnetic powder be. Then, as shown in Fig.5B, while writing words on the surface of the display sheet II with a magnet bar 9, a clear capital E appears.

Comparing the display plate II _____ with a display sheet (sold on market) under the same conditions, while writing lines slowly on both, the lines on the sheet sold on market are not clear, but the lines on the described sheet II are very clear. While writing lines fastly on both, the lines on the sheet sold on market do not appear but the lines on the described sheet II appear clearly. While erasing the words written on both, in the case of scanning slowly with a 200 gauss magnet sheet, in opposition to the display sheet sold on market in that the magnetic powder do not react to the magnet and the written words are not erased completely, the magnetic powder in the described display sheet II react fastly to the magnet so the written words disappear completely and fastly.

Example 2

According to the example 1, microcapsules of about 400

μm has been prepared and microcapsules bigger than $400 \mu\text{m}$ have been removed out. Microcapsules about $500 \mu\text{m}$ and removing particles bigger than $500 \mu\text{m}$, microcapsules about $700 \mu\text{m}$ and removing particles bigger than $700 \mu\text{m}$, microcapsules about $800 \mu\text{m}$ and removing particles bigger than $800 \mu\text{m}$, are respectively prepared, magnetic display sheet using them respectively are also produced and relations of scanning speed and erasing cleanliness and writing speed and word clearness are investigated. All of the magnetic display sheets made of gelatinized microcapsules of the invention shows good effects. In opposition to the invention, magnetic display sheet made of microcapsules from that the particles bigger than average are not cut off shows uncleanness of the written words.

Example 3

A magnetic display sheet made of microcapsules in $500 \mu\text{m}$ is prepared by the same method as example 1. While writing on the surface by a magnetic bar, clear words or pictures appear.

Example 4

A magnetic display sheet is prepared with the same method as the example 1 except dispersing the microcapsules prepared in example 1 in transparent binder of urethane resin and adding aqueous pigments (made in DAINISEI CHEMISTRY INDUSTRY INC.). The magnetic display sheet may be colored by adding pigment in

it. Many kinds of color may be possible.

Example 5

The microcapsule magnetic display sheet I as shown in Fig.6, a cross sectional view, is composed of pressure-proofing film 27, microcapsule dispersoid layer 20 thereon and then transparent film 21. The pressure-relieving film 27 and the transparent film 21 are adhered respectively by adhesives. The gelatinized microcapsules 1 used _____ are prepared by traditional method. The microcapsules are composed of magnetic powder 3 of 2% in weight that are ferrite with diameter 0.3 μ m in average and surface of them are treated by silicone oil (TAROKKUSU BL-220 in trade mark, made by CHITAN KOUGYOU INC.), nonmagnetic powder 4 of 11.6% in weight that are white titanium powders with diameter 0.3 μ m in average and the surface of them are treated by silicone oil (KRONOS(RIM)KR-330 made by CHITAN KOUGYOU INC.) and dispersion medium capsuled in the microcapsules. Particles in 400 μ m to 600 μ m are 85% in them.

The microcapsule magnetic display sheet I is made by the process of coating ink of microcapsule dispersoids on a transparent film 21 with thickness of 120 μ m and made of polyethylene terephthalate, drying it to form microcapsule dispersoid layer 20 with thickness of 600 μ m and then adhering unweaved cloth 23 with thickness of 500 μ m as pressure-relieving element 27 on the surface of the dispersoid layer.

Adhesives on the microcapsule dispersoids are not even, concave part 28 forms contact part of microcapsules themselves and adhesives 22 fill in it to stick them firmly. The microcapsule display sheet I made by the above-mentioned method has good flexibility. While writing words on surface of the magnetic display sheet I, not only the written words are clear, but also no destroyed microcapsules are discovered at repeated use.

Example 6

Microcapsule magnetic display sheet II shown in Fig.7 is made as the same as example 1. Sheet II is made by the process of forming microcapsule dispersoid layer 20 with thickness of 600 μm and adhering unweaved cloth 23 (500 μm in thickness) as the pressure-relieving element 27 that has a lining 25 of polyethylene film with thickness of 100 μm . The surface of the microcapsule dispersoid layer 20 is uneven formed by the microcapsules. The pressure-relieving element 27 is shown in Fig.8. Fig.8 is a cross-sectional view of the pressure-relieving element. Synthetic film 25 of polyethylene on the back surface of unweaved cloth 23 of the pressure-relieving element 27 is adhered by adhesives 24. Front surface of unweaved cloth 23 is covered by adhesives 22 and then a peelable film 26. While adhering the pressure-relieving element 27 to the uneven surface of the microcapsule dispersoid layer 20, peeling off the film 26. The sheet II obtained here has a good strength as the adhesives 22 fill the concave parts of the microcapsule

dispersoid layer 20 and stick to it firmly without gap. While writing on the surface of the microcapsule display sheet obtained in the example 2 as the same as in example 1, it is clarified that the sheet has a good durability without destroyed particles and the lining 25 of polyethylene film makes no influence on erasing operation.

Example 7

Microcapsule magnetic display sheet is made by the same process as example 6 except adding aqueous colorant (NEW LACTISUM in trade mark, made by DAINISEI CHEMISTRY INC.) in aqueous adhesives 2 of the microcapsule dispersoid layer of the microcapsule display sheet II. By adding colorants in element, the sheet may be colored in many ways.

Example 8

As shown in Fig.9, in stead of the pressure-relieving element 27 of the microcapsule display sheet I made in example 1, adhering polyethylene terephthalate 32 with thickness of 150 μm by acryl emulsion adhesives to form adhesive layer 31 and to produce the microcapsule display sheet III. While writing on the surface of the microcapsule display sheet III as the same as in example 1, it is clarified that the sheet has a good durability without destroyed particles and the lining 32 of polyethylene film makes no influence on erasing operation.

Example 9

Adding silica as filler in adhesives to form

pressure-relieving element, then adhering the polyethylene terephthalate by adhesives to form adhesive layer to produce the microcapsule display sheet III as the same as in example 8. The thickness of the adhesive layer is about $50 \mu\text{m}$. While writing on the surface of the microcapsule display sheet III as the same as in example 5, it is clarified that the sheet has a good durability without destroyed particles and the lining 32 of polyethylene film makes no influence on erasing operation.

Example 10

Microcapsule display sheet I is made by the same process as example 5 except the thickness of the transparent film being $50 \mu\text{m}$, $80 \mu\text{m}$, $100 \mu\text{m}$, $180 \mu\text{m}$. The microcapsule display sheet with $50 \mu\text{m}$ thickness of transparent film I is suitable to be connected to computer and that with $180 \mu\text{m}$ thickness of transparent film is desirable to be used for children at young age. The microcapsule display sheet II described in example 6 is also produced and the effects are the same.

Example 11

Microcapsule display sheet I is made by the same process as in example 5 except the thickness of the unweaved cloth being $50 \mu\text{m}$, $120 \mu\text{m}$, $150 \mu\text{m}$, $180 \mu\text{m}$, $200 \mu\text{m}$, $250 \mu\text{m}$, $300 \mu\text{m}$, $340 \mu\text{m}$, $420 \mu\text{m}$ respectively. The microcapsule display sheet with $50 \mu\text{m}$ thickness of the unweaved cloth is suitable to be

connected to computer and that with 400 μ m thickness of the unweaved cloth is desirable to be used for children at young age. The microcapsule display sheet II described in example 6 is also produced and the effects are the same.

Example 12

Microcapsule display sheet III is made by the same process as in example 8 except the thickness of the synthetic film being 50 μ m, 80 μ m, 100 μ m, 125 μ m, 180 μ m, 200 μ m respectively. The microcapsule display sheet with 50 μ m thickness of the synthetic film is suitable to be connected to computer and that with 200 μ m thickness of the synthetic film is desirable to be used for children at young age.

Example 13

Microcapsule display sheet III is made by the same process as in example 8 except the thickness of the synthetic film being 150 μ m and thickness of adhesive layer being 30 μ m and 80 μ m respectively. The microcapsule display sheet with 30 μ m thickness of the adhesive layer is suitable to be connected to computer and that with 200 μ m thickness of the unweaved cloth is desirable to be used for children at young age.

Features of the described microcapsule magnetic display sheet and method for producing a microcapsule magnetic display sheet are claimed in the Applicant's co-pending UK Patent Application No. 9516173.3.

WHAT IS CLAIMED IS:

1. Gelatinized microcapsules for magnetic display in which dispersion medium, magnetic powder and nonmagnetic powder are enclosed, characterized in that said dispersion medium in the microcapsules comprise at least a low boiling point solvent and the average particle diameter of the microcapsules is in a range of $200 \mu\text{m}$ to $800 \mu\text{m}$.
2. The gelatinized microcapsules for magnetic display according to claim 1, characterized in that said dispersion medium contains a high boiling point solvent having a boiling point higher than 175°C .
3. The gelatinized microcapsules for magnetic display according to claim 1 or 2, characterized in that said dispersion medium includes a dispersant therein.
4. The gelatinized microcapsules for magnetic display according to any one of claims 1 to 3, characterized in that a suspension is contained in the dispersion medium.
5. The gelatinized microcapsules for magnetic display according to any one of claims 1 to 4, characterized in that said dispersion medium is a mixture of high boiling point alcohol-based compound and low boiling point solvent.
6. The gelatinized microcapsules for magnetic display according to any one of claims 1 to 5, characterized in that said magnetic powder is affinity-treated.
7. The gelatinized microcapsules for magnetic display

according to any one of claims 1 to 6, characterized in that said nonmagnetic powder is affinity-treated.

8. The gelatinized microcapsules for magnetic display according to any one of claims 1 to 7, characterized in that among said microcapsules, those having particle diameter bigger than the average particle diameter are removed.

9. The gelatinized microcapsules for magnetic display according to any one of claims 1 to 8, characterized in that the particles essentially being size of $400 \mu m \pm x \mu m$ to $800 \mu m \pm x \mu m$ (wherein $x = 10$ to 20).

10. Gelatinized microcapsules substantially as herein described with reference to the accompanying drawings.



The
Patent
Office

Application No: GB 9810767.5
Claims searched: 1-10

Examiner: Graham Russell
Date of search: 14 August 1998

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): B6P (PMAB)

Int Cl (Ed.6): B43L 1/00

Other: Online: EDOC, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
	None	

36

- | | |
|---|--|
| X Document indicating lack of novelty or inventive step | A Document indicating technological background and/or state of the art. |
| Y Document indicating lack of inventive step if combined with one or more other documents of same category. | P Document published on or after the declared priority date but before the filing date of this invention. |
| & Member of the same patent family | E Patent document published on or after, but with priority date earlier than, the filing date of this application. |